A High-Performance Recycling Solution for PolystyreneAchieved by the Synthesis of Renewable Poly(thioether) Networks Derived from D -Limonene

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Question	Response
Please submit a plain text version of your cover letter here. If you are submitting a revision of your manuscript, please do not overwrite your original cover letter. There is an opportunity for you to provide your responses to the reviewers later; please do not add them here.	Dear Dr. Gregory: We are pleased to submit our communications article entitled "A High-Performance Recycling Solution for Polystyrene Achieved by the Synthesis of Renewable Poly(thioether) Networks Derived from D-Limonene" for consideration for publication in Advanced Materials. We are excited to report what we believe is a novel approach to sustainable materials development that is based upon a new strategy for thermoplastic polymer recycling with a notable advancement in renewable polymer synthesis. This work is built upon the premise that the development of new sustainable materials with increased inherent value (i.e., well-engineered, value-driving material properties) is possible through innovative design at the materials engineering level. In the solvent-based material recycling process described in our manuscript, D-Limonene functions simultaneously both as a solvent for dissolving polystyrene (PS) waste and as a monomer that undergoes UV-catalyzed thiol-ene polymerization reactions with polythiol co-monomers to afford polymeric products comprised of precipitated PS phases dispersed throughout elastomeric poly(thioether) networks. By varying the amount of recycled PS additives, which were taken from expanded polystyrene (EPS) waste cups provided by a major U.S. fast food company, we achieve tailorability of microstructural morphology, modulus, toughness, tensile strength and strain capacity in order to demonstrate a broad application range for the new material system. We believe that this work marks the first instance in which the successful bulk synthesis and mechanical characterization of network polymers comprised solely of D-limonene and polythiol co-monomers are reported in the literature. Furthermore, the demonstrated synthetic utility of this naturally-derived polymer system as a new PS recycling strategy provides a unique materials-based avenue to achieving environmental sustainability while combining non-renewable and renewable materials to produce blended networks that exhibit mechanical properties that greatly exceed those of either polystyrene or the poly(thioether) network homopolymers individually. The authors recommend Profs. Christopher N. Bowman, christopher.bowman@colorado.edu, Craig J. Hawker, hawker@mrl.ucsb.edu and Andrew B. Lowe, a.lowe@unsw.edu.au as reviewers for this manuscript. These researchers have been leaders in implementing thiol-ene chemistry in advanced materials applications and are well-suited to serve as reviewers for this manuscript. Please do not hesitate to contact us if any issues arise surrounding the submission of this manuscript. Best Regards, Keith Hearon
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As consumer demands drive increased global production of plastic products and waste, the need for innovative strategies for improving environmental sustainability continues to grow. As long as non-environmentally degradable plastics are produced, the development of improved recycling techniques must continue in order to decrease additional material consumption and to reduce non-degradable plastic waste content in landfills.[1] There is hope that progress in polymer science will eventually give rise to alternative plastic materials that may eliminate the need for the production of petroleum-based and other non-degradable plastics altogether, and recent studies have investigated the development of naturally based polymers, such as polycarbonates derived from coffee extracts,[2] terpene-[3] and fatty acid-derived[4] heteropolymers and cellulose-based polymer composites,[5] among others. One drawback that often surrounds sustainable materials development is the seemingly pervasive notion that improving the environmental suitability of materials comes with a sacrifice in material functionality.[6] Studies reporting material selection strategies often weigh material capabilities against environmental sustainability,[7] and recycling processes in general are assumed to bring about some degree of material deterioration.[8] This work is built upon an alternative premise, that the development of new sustainable materials with increased inherent value (i.e., well-engineered, value-driving material properties) is possible through innovative design at the materials engineering level. We report a novel approach to sustainable materials development that is based upon a new strategy for thermoplastic polymer recycling with a notable advancement in renewable polymer synthesis. By combining petroleum-derived polymers with bio-based monomer feedstocks, biphasic, blended polymer products are produced and are shown to exhibit facile tunability of physical and material properties. This one-pot, solvent-based recycling approach yields neat recycled products without the use of solvent evaporation or solute precipitation, and the functional utility of the resulting polymer blends greatly exceeds that of either homopolymer alone.

Reported herein is a new method for recycling polystyrene (PS), in which special consideration is given to expanded polystyrene (EPS) waste used in food and beverage packaging applications. The difficulties associated with EPS recycling have been widely publicized. It is estimated that over 3 million tons of EPS are produced each year globally, with roughly 70% of EPS products being single-use food and beverage packaging.[9] Because both transporting low-density EPS waste and cleaning it to remove contaminant residue greatly increase cost and time required for EPS recycling, an overwhelming majority of food-contaminated EPS waste is not recycled.[10] The simplest and most common method of recycling EPS is material recycling by mechanical compaction, and mechanical EPS densifiers are commercially available from multiple sources.[11] Since mechanical densifiers require that EPS be contaminant free before compaction, mechanical densification is not ideal for recycling food or drink contaminated waste items. Solvent-based material recycling has been shown to be tolerant of some contaminated EPS substrates because many contaminants are insoluble in solvents that dissolve EPS and can be removed using coarse filtration after EPS dissolution.[12] The solubility and behavior of EPS in multiple solvents has been previously reported.[13] In the late 1990's and early 2000's Sony Corporation instituted a solvent-based recycling effort in Japan, in which the citrus fruit extract D-limonene, which dissolves polystyrene, was used to recycle EPS waste. Sony's report of this recycling process is extremely in-depth, but this recycling effort appears to have been abandoned sometime between 2004 and 2006.[14] Considering the low inherent value of recycled polystyrene, Sony's apparent decision to cease this recycling effort may have been financially motivated.

The primary novelty in the present study stems from the idea that D-limonene can both dissolve polystyrene, as first demonstrated by Sony Corporation, and can also function as a diene monomer in thiol-ene reactions. Thiol-ene "click" chemistry is a powerful synthetic tool that is being implemented in increasingly diverse areas of polymer science.[15] The reaction between C=C and SH functional groups, which is often UV catalyzed but can also

proceed under elevated temperature conditions, is highly efficient, tolerant of many functional

groups, and capable of proceeding under mild conditions.[16] A number of network polymers

have been prepared from polyfunctional alkene and polythiol monomers and utilized in

applications ranging from medical to commodity devices.[17] D-Limonene, shown in **Figure 1**,

consists of two C=C groups and is, theoretically, capable of functioning as a monomer in

thiol-ene polymerization reactions with a co-monomer such as trimethylolpropane tris(3-

mercaptopropionate) (TMPTMP). A poly(thioether) network synthesized from D-limonene

would thus be, by definition, derived from a naturally-occurring precursor. We observed that

at temperatures near 25 °C, D-limonene and TMPTMP mixtures are immiscible, although

brief 365 nm UV irradiation and/or heating eventually results in the formation of a

homogeneous solution that can be transferred to a mold without further network formation

occurring until subsequent exposure to UV irradiation. Previous studies have reported the

synthesis of polymers through multi-step processes in which D-limonene is first functionalized

and then subjected to various methods of polymerization,[18, 19] and in a recent study, the

reactivities of the double bonds in limonene with various thiol groups are reported.[20]

However, to our best knowledge, none of these studies has reported the bulk thiol-ene

polymerization and thermomechanical characterization of a network polymer consisting

solely of D-limonene and a polythiol co-monomer. The ester linkages in TMPTMP also

afford the synthesis of a poly(thioether) network that is biodegradable, and Claudino, *et al.*

have noted this concept and proposed the use of limonene-*co*-poly(mercaptopropionate)

networks as synthetic materials for degradable tissue scaffolds.[20]

Because of the flexible nature of the thioether linkage, many poly(thioether) networks

are elastomeric and possess poor mechanical integrity at and above 25 °C.[21] Such

elastomeric behavior was predicted for the D-limonene-based network homopolymer whose

synthesis is shown in **Figure 1** and was observed upon neat polymer synthesis and handling.

The addition of PS additives to this poly(thioether) network was predicted to increase

modulus and improve toughness and mechanical strength, and the synthesis of biphasic polymer blends comprised of PS additives dispersed in limonene-co-polythiol networks was therefore attempted both to improve network mechanical integrity and to demonstrate a new method of PS recycling. It is well-known that the functional utility of PS can be increased by the synthesis of PS/rubber blends or co-polymers, and high impact polystyrene (HIPS) can be prepared by dissolving a thermoplastic such as polybutadiene in styrene and curing the solution to produce biphasic materials. These polymers possesses improved mechanical strength and toughness in comparison with that of PS.[22] Other studies have reported the synthesis, microstructural imaging, and thermomechanical characterization of other thermoset/thermoplastic heteropolymer blends, including PMMA, PS and polyurethane additives in polyester network matrices[23] and polyetherimide additives in epoxy network matrices.[24] To our best knowledge, a polymer blend comprised of a thermoplastic additive dispersed in poly(thioether) matrix has yet to be reported.

The novel process reported herein enables the simultaneous densification, purification, and reclamation of food or beverage-contaminated EPS waste. As shown in **Figure 2(a)**, food or drink-contaminated EPS waste can first be immersed in a reservoir containing D-limonene. After mixing and EPS dissolution in D-limonene, a liquid bilayer forms. In the last image in **Figure 2(a)**, the bottom layer consists of Coca-Cola™ and the top layer consists of an EPS cup provided by Chick-fil-A, Inc. dissolved in D-limonene ($M_w \sim 396$ kDa). Through basic extraction, the bottom layer contaminants can be drained, and upon coarse filtration, a purified solution of polystyrene in D-limonene remains. As shown in **Figure 2(b)**, reclamation of polystyrene is achieved by addition of polythiol co-monomer and photoinitiator and subsequent heating to 140 °C, which results in a homogeneous dissolution of all species. Pouring of this hot solution into a pre-heated mold and subsequent UV irradiation causes the formation of an elastomeric poly(thioether) network, after which phase separation of polystyrene proceeds, producing dispersed polystyrene microphases and/or

nanophases throughout the network. Demonstrating the change in optical behavior from transparency to opacity that occurs upon PS heterophase addition to D-limonene-co-polythiol networks, macroscale images of D-limonene-*co*-TMPTMP films containing 0% and 30% PS additives are provided in **Figure 2(c).** The iPhone 4™ protective case prototype pictured in **Figure 2(b)** was fabricated to demonstrate the processability of these new materials into a geometry representative of that of a potential industrial application.

We synthesized blended polymers containing recycled PS additives dispersed in D-limonene-*co*-polythiol network matrices to create a series of polymer blends with greater toughness than either homopolymer exhibits individually. D-Limonene functions simultaneously as a solvent for dissolving polystyrene (PS) waste and as a monomer that undergoes UV-catalyzed thiol-ene polymerization reactions with polythiol co-monomers to afford polymeric products comprised of precipitated PS phases dispersed throughout elastomeric poly(thioether) networks. By varying PS additive composition, we sought to achieve tailorability of microstructural morphology, modulus, toughness, tensile strength and strain capacity in order to demonstrate a broad application range for the new material system. We believe that this work marks the first instance in which the successful bulk synthesis and mechanical characterization of network polymers comprised solely of D-limonene and polythiol co-monomers are reported in the literature, and the demonstrated synthetic utility of this naturally-derived polymer system as a new PS recycling strategy provides a unique materials-based avenue to achieving environmental sustainability, while combining non-renewable and renewable materials to produce blended networks that exhibit remarkable mechanical properties.

In order to understand the effects of increasing PS additive composition on microstructural morphology, SEM images of samples containing 0, 10, 20, and 30% overall weight fraction PS were taken and are provided at 3000x magnification in **Figure 3.** For the SEM images in **Figure 3**, the samples were prepared by immersion in liquid nitrogen, cold

fracturing, attempted thermoplastic PS phase extraction using dichloromethane, sample drying, and gold sputtering prior to imaging. Consequently, the more lightly-colored phases in **Figure 3** correspond to poly(thioether) networks, and any cavities shown represent empty space that corresponds to extracted thermoplastic PS phases. In general, poly(thioether) network phases appear to decrease in average size with increasing PS composition, although the specific morphologies corresponding to the varying PS phases are notably different in nature. In **Figure 3(a)**, 0% PS shows only a single poly(thioether) phase, and in **Figure 3(b)**, 10% PS shows what appear to be ~3-5 μm sized cavities corresponding to PS phases that were dispersed throughout a network matrix similar to that shown in **3(a)**. In **Figure 3(c)**, 20% PS appears to have generated a bimodal microstructural morphology with spherical ~3μm network phases and cavities that could correspond to PS microphases of similar size and geometry. In **Figure 3(d)**, the network obtained following extraction of the 30% PS composition appears to exhibit a bimodal microstructure with spherical network and PS phases that are sub-micron in size and of similar homogeneity and distribution to the 20% PS sample in **3(c)**. Our interpretation of the SEM images is limited to a qualitative assessment to confirm that phase segregation had occurred uniformly throughout the matrix material, as quantitative interpretation is complicated by potential perturbations to the initial blended networks during the processing steps.

While SEM provides some insights into the microstructure of the bulk phase, direct evaluation of the surface morphology of the composite system was also performed. Given the importance of exposed-face character to mold release properties, bioactivity and tribological response, it is critical to assess the intrinsic phase behavior and topography at the surface. To provide such characterization, atomic force microscopy (AFM) of the composite systems at 0, 10, 20 and 30% PS weight fraction were obtained. Topographic maps of the micrographs of the assessed systems are provided at two separate scales, 20 μm × 20 μm and 3 μm × 3 μm and are provided in **Figure 3(e)**. The 3 μm × 3 μm rendering also has phase contrast overlaid

to elucidate phase boundaries where present. While generally following the trends observed in SEM, the findings for this series can be summarized as follows: (1) 0% PS displayed a small amount of residual processing residues, exhibited exceptional flatness with shallow pitting (*ca*. 10 nm deep) and had no indication of intrinsic phase boundaries, (2) 10% PS displayed some PS sheeting at the microscale, similar to the gaps observed by SEM and possessed *ca*. 500 nm PS phase domains at smaller scale, (3) 20% PS displayed the largest microscale heterogeneity, exhibited the roughest surface morphology of the samples observed, had pitting and protrusions consistent with the scale of the features observed in the solvent etched PS SEM figures, and displayed microscale phase separation wherein the PS domain expressed smaller sub-domains on scales similar to that observed in the 10% PS system, and (4) the 30% PS sample presented an overall more homogeneous surface on the microscale with periodic large protrusions which appeared to be surface buckling; in the homogeneous regions, fully isolated PS nanodomains (<200 nm) saturated the landscape.

To determine the effects of increasing polystyrene composition on the thermomechanical behavior of the D-limonene-*co*-TMPTMP networks imaged in **Figure 3**, dynamic mechanical analysis (DMA) experiments were run in tension on 0, 10, 20, and 30 wt% PS samples. **Figure 4(a)** shows plots of storage modulus *versus* temperature for D-limonene-*co*-TMPTMP, -PETMP, and -DPEHMP networks. The increase in rubbery modulus from TMPTMP to PETMP-based networks as polythiol functionality increases from 3 to 4 is expected and indicates an increase in crosslink density with increased monomer functionality. The lack of an increase in rubbery modulus from PETMP to DPEHMP as functionality increases from 4 to 6 is most likely the result of poor monomer miscibility and high DPEHMP viscosity, which could prevent the reaction of functional groups and prevent network formation. **Figures 4(b), 4(c) and 4(d)** show DMA characterization data for D-limonene-*co*-TMPTMP networks containing varying PS additive compositions. Plots of **(b)** storage modulus, E', **(c)** loss modulus, E'', and **(d)** tangent delta *versus* temperature for each

PS composition are shown, and each PS-containing rubber whose DMA is shown in **Figures 4(b-d)** exhibits a thermal transition below -10 °C that is consistent with the glass transition of the D-limonene-*co*-TMPTMP poly(thioether) network and also exhibits a thermal transition near 100 °C that is consistent with the glass transition of polystyrene. As polystyrene composition increases, the storage and loss modulus of each sample increase with a clear trend at temperatures between the glass transition of the rubber network and the glass transition of polystyrene. **Figure 4(e)** shows that both E' and E'' increase roughly two orders of magnitude at 25 °C as PS composition is increased from 0 to 30%. The toughening effect that arises from creating a material with combined glassy and rubbery phases is demonstrated in **Figure 4(f)**, which shows average strain-to-failure data for 0%, 30% and 100% PS D-limonene-*co*-TMPTMP samples at 25 °C. While the 100% PS material exhibits brittle behavior at 25°C and fails at 1.8% strain and the 0% PS material exhibits weak elastomeric failure and fails at a stress of 1.2 MPa, the 30% PS material exhibits a more ductile behavior and fails at 55% strain while also exhibiting a failure stress greater than 12 MPa. While the average toughness of the 100% PS sample at 25 °C was 0.34 ± 0.06 MJ/m^3 and that of the 0% PS sample was 0.13 ± 0.02 MJ/m^3, that of the 30% PS sample was 5.03 ± 0.82 MJ/m^3. This increase in toughness at 25°C of more than an order of magnitude in comparison with that of either homopolymer is promising, and a toughness of ~5 MJ/m^3, while lower than that of poly(acrylonitrile-*co*-butadiene-co-styrene (ABS) and some other high-performance HIPS resins reported in the literature, actually exceeds reported toughness values for a number of HIPS materials.[25] The thermomechanical behavior as a function of PS fraction, taken in conjunction with the micro- and nano-domain features observed for the PS phase in this series by SEM and AFM, indicate that the observed toughening for the 30% PS material can be explained by the existence of a high number of nanodomains, which allow expression of a large surface to volume ratio for the PS fraction.

In this work, we report a multicomponent process for sustainable materials development that combines an innovative polystyrene recycling technique with a breakthrough achievement in renewable polymers synthesis to afford a new polymer system with tunable physical and material properties. Through a well-engineered material design strategy, blended polymeric materials comprised partly of recycled thermoplastic PS components and partly of D-limonene-derived poly(thioether) network components exhibit mechanical integrity that greatly exceeds that exhibited by either component alone. By varying PS composition between 0 and 30 wt %, storage modulus at 25°C can be tuned over the range of 1 to 370 MPa, and these materials consequently may be suitable for use in a diverse array of polymeric applications. One set of applications that appears promising is that of impact resistant polymers, and the fabrication of a cellular phone protective case prototype was demonstrated in this work to provide an example of one potentially well-suited industrial application. Future studies will investigate the effects of various synthetic conditions on the microstructures of the biphasic materials to provide a basis for determining structure-property relationships, and further characterization of thermomechanical properties, tensile behavior, and impact strength will then be used to identify trends relating material structures to mechanical properties.

Concerning the significance of this work with respect to the broader scope of renewable materials development, this work demonstrates that environmental suitability in new polymers can be achieved without sacrificing functional utility. If innovative material design were to become a staple component of sustainable materials development, the scientific community could produce new classes of materials that excel from both environmental stewardship and material functionality standpoints. Concerning the significance of the specific process for preparing naturally-derived polymers from D-limonene that is reported, a number of studies have stated the potential significance of such naturally inspired network polymers for use in soft polymer applications[19] (and in implantable tissue applications in the case of D-limonene-

co-poly(mercaptopropionate) networks).[20] While previous studies have provided excellent groundwork for limonene-based poly(thioether) synthesis using a "ground-up chemistry-based approach," we have chosen to address terpene-derived polymer synthesis instead from a "top-down materials synthesis approach," in which bulk materials are first synthesized, mechanically characterized and evaluated on material grounds for potential industrial relevance. This work should complement previous chemistry-focused works very well and should provide a unique perspective on terpene-derived polymer synthesis.

Supporting Information

Supporting Information is available online from the Wiley Online Library or from the author.

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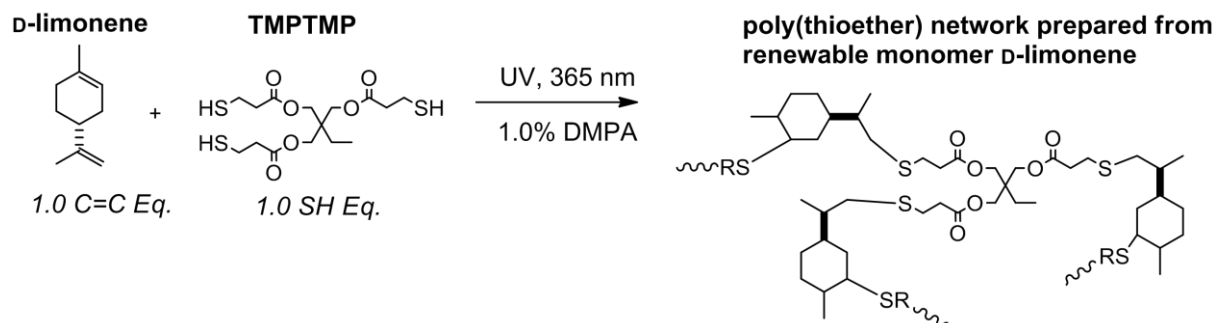
Figure 1. Synthetic approach for the preparation of poly(thioether) networks derived from D-limonene and the polythiol TMPTMP

(a)

(b)

(c)

Figure 2. (a) Simultaneous densification and purification of beverage-contaminated EPS waste cup containing 300 mL of Coca-Cola™. The cup completely dissolves in D-limonene, and separation of the Coca-Cola waste contaminant layer from the polystyrene/limonene solution occurs immediately after stirring is stopped; (b) Successful fabrication of iPhone 4™ protective case prototype made from D-limonene-*co*-TMPTMP +30% PS additive demonstrates processability of D-limonene-based poly(thioether) networks with recycled PS additives into a geometry representative of that of one potential industrial application; (c) Macroscale images of 0% PS (*top*) and 30% PS (*bottom*) D-limonene-*co*-TMPTMP network polymer films
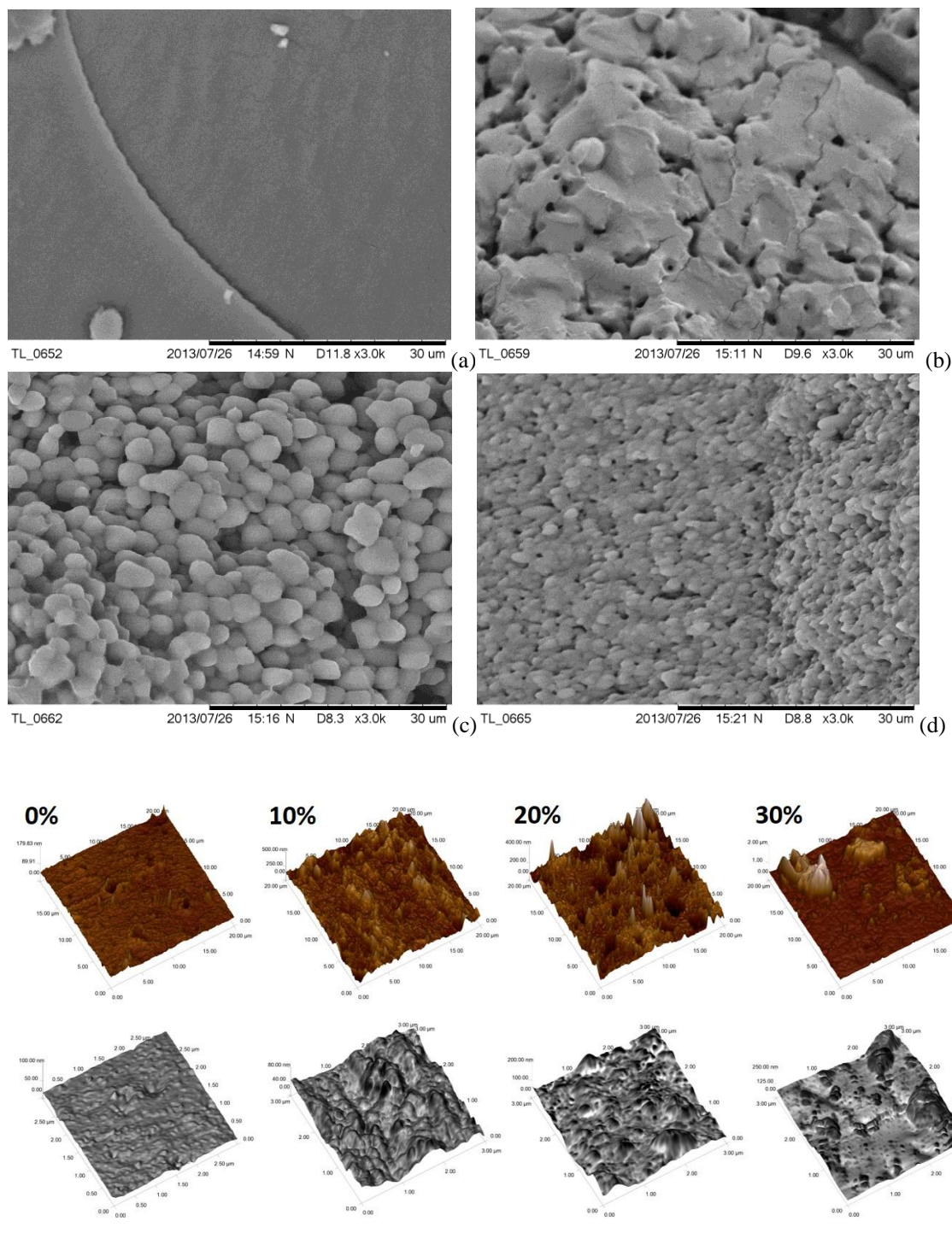
14   14

Figure 3. (a-d) SEM images taken at 3000x magnification showing microstructures of D-limonene-*co*-TMPTMP networks containing PS weight fractions of (a) 0%; (b) 10%; (c) 20%; (d) 30%. All scale bars are 30 μm. Prior to SEM imaging, samples were immersed in liquid nitrogen and fractured, immersed in dichloromethane to extract the PS phases, dried, and gold sputtered; (e) AFM Micrographs of 0-30% PS wt/wt D-limonene-*co*-TMPTMP networks. Top: 3D topography for a 20 μm × 20 μm area. Bottom: 3 μm × 3 μm area with topography (3D) overlaid with a grey scale rendering of the phase contrast image (range ±5° in all images).
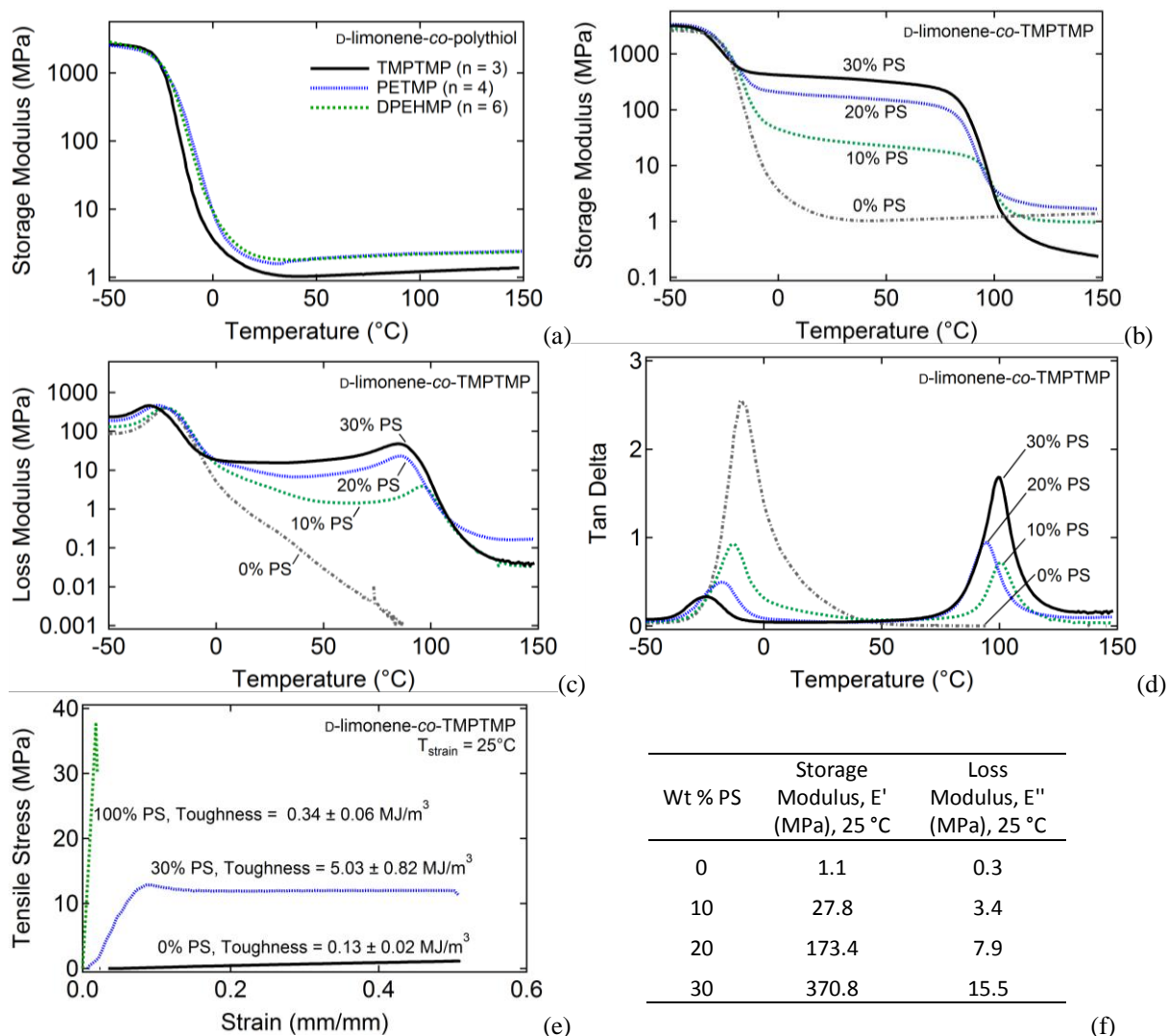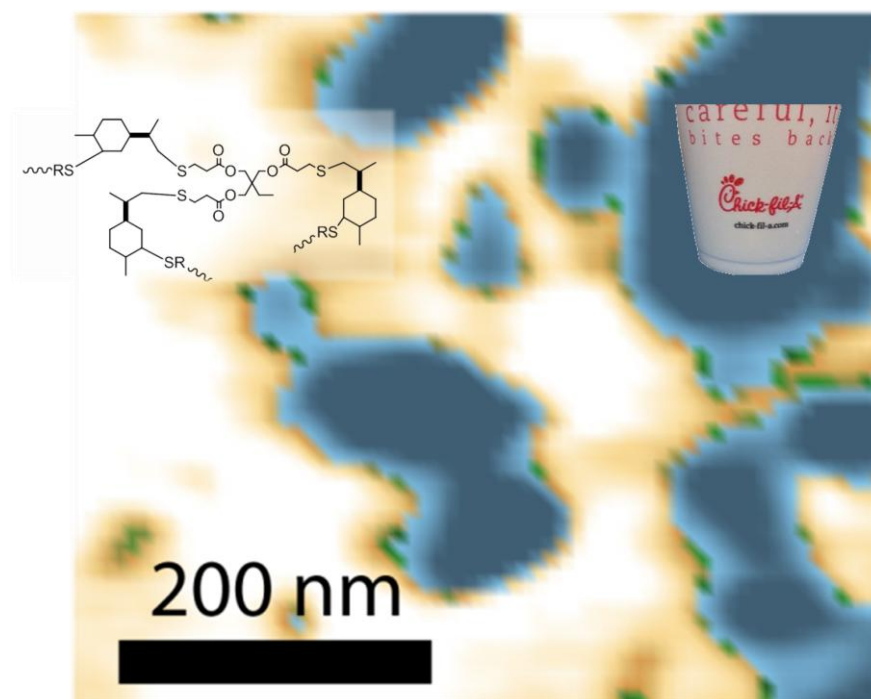
Figure 4. (a) DMA data showing plots of storage modulus versus temperature for D-limonene-*co*-TMPTMP, PETMP, and DPEHMP network polymers indicate network thermomechanical behavior for all three samples; DMA data showing (b) storage modulus, E', (c) loss modulus, E'', and (d) tangent delta for samples containing 0, 10, 20, and 30%; (e) strain-to-failure data showing an order of magnitude higher toughness for 30% PS blends in comparison with that of 0% and 100% neat polystyrene; (f) table showing effect of increased PS composition on storage modulus, E', and loss modulus, E'', at 25°C

16   16

Nanocomposite polymers have been prepared using a new sustainable materials synthesis process in which D-Limonene functions simultaneously both as a solvent for recycling polystyrene (PS) waste and as a monomer that undergoes UV-catalyzed thiol-ene polymerization reactions with polythiol co-monomers to afford polymeric products comprised of precipitated PS phases dispersed throughout elastomeric poly(thioether) networks. These blended networks exhibit mechanical properties that greatly exceed those of either polystyrene or the poly(thioether) network homopolymers alone.

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Supporting Information

A High-Performance Recycling Solution for Polystyrene Achieved by the Synthesis of Renewable Poly(thioether) Networks Derived from d-Limonene

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Experimental Section

Polymer synthesis: Functional equivalents totaling 10 g of D-limonene (TCI America, >95%,) trimethylolpropane tris(3-mercaptopropionate), pentaerithritol tetrakis(3-mercaptopropionate) (Sigma Aldrich, >95%), and/or dipentaerithritol hexakis(3-mercaptopropionate) (Wako, >97%) were massed in glass vials, and 1 wt% 2,2'-dimethoxy-2-phenylacetophenone (DMPA) (Sigma Aldrich, >99%) photoinitiator was added. EPS powder, which was ground from EPS cups provided by Chick-fil-A, Inc. (CFA), was added to the monomer mixtures in varying quantities so as to formulate mixtures with polystyrene compositions of 0, 10, 20, and 30% overall weight fraction. The monomer and EPS mixtures were not miscible initially and were heated to 140°C for 2 h, after which the formation of homogeneous solutions occurred, as shown in **Figure 2**. The resulting solutions exhibited viscosity increases with increasing EPS composition. Neat films were cast by injecting the hot solutions inside glass molds pre-heated to 140°C. The injections were carried out inside a vacuum oven heated to 140°C. The hot glass molds were then immediately removed from the oven, placed in a UVP CL-1000L 365 nm UV crosslinking chamber, and exposed to 365 nm UV irradiation for 1 h. Within 10-20 seconds of UV exposure, the clear homogeneous solutions inside the glass molds began to

turn white, apparently undergoing polystyrene phase separation brought on by either

poly(thioether) network formation, cooling temperatures, or both factors. The resulting films

became completely white within 1-2 min. After 1 h, the cured films were post-cured at 130°C

at 1 torr for 24 h. Without polystyrene, the poly(thioether) networks were amorphous,

optically clear rubbers, and the addition of PS resulted in the formation of opaque materials,

as shown in **Figure 2(c).**

Polystyrene molecular weight characterization: To determine the average molecular weight

of EPS samples taken from EPS CFA cups, gel permeation chromatography (GPC)

measurements were conducted using a tetrahydrofuran GPC system equipped with a Waters

Chromatography (Milford, MA) model 1515 isocratic pump, a model 2414 differential

refractometer, and a three-column set of Polymer Laboratories (Amherst, MA) Styragel

columns (PL$_{gel}$ 5 μm Mixed C, 500 Å, and 104 Å, 300 _ 7.5 mm columns). The system was

equilibrated at 35 °C in tetrahydrofuran, which served as the polymer solvent and eluent (flow

rate set to 1.00 mL/min). Polymer solutions were prepared at a known concentration (ca. 3

mg/mL), filtered with a 0.2 micron PTFE mesh filter, and an injection volume of 200 μL was

used. Data collection and analyses were performed with Precision Acquire software and

Discovery 32 software (PrecisionDetectors). The differential refractometer was calibrated

with standard polystyrene materials (SRM 706 NIST). The average M_n, M_w, and PDI were

150 kDa, 396 kDa, and 2.635, respectively.

Microstructural imaging by scanning electron microscopy: SEM imaging was used to

understand the effects of increasing PS composition on microstructural morphology. SEM

samples were prepared by immersion of ~100 mg samples in liquid nitrogen for 30 s, cold

fracturing by hand, attempted thermoplastic PS phase extraction by immersion of fractured

~50 mg samples in 100 mL dicholoromethane and light vortexing for 48 h using a LabConco

RapidVap apparatus at vortex setting 15 and at ambient temperature and pressure, drying of DCM-swelled samples at 50°C at 1 torr for 48 h, and gold sputtering with a Cressington 108 sputter coater, model 6002-8 (Ted Pella, Inc., Redding, CA) for 60 s at a height of 3 cm, prior to imaging. All samples were imaged on the fractured faces at 25, 500, and 3000x magnification using a Hitachi TM3000 Tabletop Microscope (Hitachi High Technologies America, Inc. Nanotechnology Systems Division, Dallas, TX), with a filament current set to 1750 mA. Software used to acquire the images was Bruker Quantax 70 Microanalysis Software package (Bruker Nano GmbH, Berlin, Germany).

Atomic Force Microscopy

AFM micrographs of the system were taken with an Asylum 3D-SA atomic force microscope operated in tapping mode at 142 kHz, a nominal drive voltage of 500 mV. A silica nitride probe was used with k = 40 N/m (Vista Probes) and a nominal tip diameter of 10-15 nm as reported by the manufacturer. Sample preparation included a fast rinse of the samples (0%, 10%, 20% and 30% PS) with a 25% by volume aqueous ethanol solution (<5 seconds) followed immediately by drying under a dry, filtered nitrogen gas flow for *ca.* 10 minutes and fixture to a glass slide.

Dynamic mechanical analysis: DMA experiments were performed on triplicate samples using a TA Instruments Q800 Dynamic Mechanical Analyzer in the DMA Multifrequency/Strain mode in tension using a deformation of 0.1% strain, a frequency of 1 Hz, a force track of 150%, and a preload force of 0.01 N. Each experiment was run from -50 to 150°C using a heating rate of 2°C/min on $4.0 \times 25.0 \times 0.75$ mm rectangular samples, which were machined using a Gravograph LS100 40 W CO_2 laser machining instrument.

Uniaxial tensile testing: ASTM Type V dog bone samples were machined using a Gravograph LS100 40 W CO2 laser machining device. All laser machined samples except for the rubbery 0% PS samples were sanded around the edges using 400, 800 grit sandpaper. Strain-to-failure experiments were conducted at 25°C in a temperature chamber that utilizes forced convection heating on 0% and 30% samples synthesized in this study and on 100% PS samples (McMaster-Carr, M_w ~ 350 kDa) on $n \geq 5$ specimens for each sample. There experiments were conducted using an Instron Model 5965 electromechanical, screw driven test frame equipped with a 500 N load cell and 1 kN high temperature pneumatic grips. An Instron Advanced Video Extensometer with a 60 mm field-of-view lens optically measured the deformation of the samples by tracking parallel lines applied at the ends of the gauge length. The samples were heated to 25°C under zero load (unclamped bottom grip). The temperature was held for 10 min to allow for thermal equilibrium to be reached, after which the bottom grip was clamped, and then experiments were started thereafter using a deformation rate of 10 mm/min. Data were recorded using Instron Bluehill 3 software.

Prototype cell phone case fabrication: A positive mold with geometric dimensions approximately representative of those of a protective case made to fit an Apple iPhone 4™ cellular device was designed using SolidWorks software. Using a Stratasys Fortus 360mc 3D printer, positive molds were printed using the Stratasys base-soluble resin. Each printed positive molds was then placed in pre-assembled 2"× 6"× 4" acrylic molds and attached to the bottom of the mold using super glue. Pre-mixed silicone Sylgard 184™ base and curing agent were then poured over the printed molds and evacuated at 1 torr at 25°C for 5 min, after which a smooth surface layer was observed. The silicone mold was then cured at 50 C for 4 h. The printed resin was dissolved out of the silicone mold by etching in 0.1 N NaOH solution using the Stratasys base bath for 72 h. The resulting silicone mold contained a negative image of an Apple iPhone 4™ case. This silicone mold and 50 g of functional equivalents of

limonene and TMPTMP with 30 wt% PS additive were pre-heated to 140°C for 2 h. The

dissolved PS solution was then poured in the oven into the silicone mold. The molded

solution was then moved into a UVP CL-1000L 365 nm UV crosslinking chamber, exposed

to UV irradiation for 1 h, and post-cured at 130°C at 1 torr for 24 h.